The Effect of Adjacent Unshared Electron Pairs on Ease of Carbanion Formation[1]

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Abstract: The kinetics of sodium methoxide catalyzed deuterium exchange of methyl cyclopentanecarboxylate, two of its oxa derivatives, and their acyclic analogs were studied in methanol-*O-d* solution. At 35° methyl cyclopentanecarboxylate exchanged 13 times as fast as methyl α-ethylbutyrate, methyl tetrahydrofuran-2-carboxylate exchanged four times as fast as methyl α-methoxybutyrate, and methyl 1,3-dioxolane-2-carboxylate exchanged half as fast as methyl dimethoxyacetate. From these results it was concluded that rates of carbanion formation may be decreased by repulsions between the unshared electron pairs of the carbanionic carbon atom and those of oxygen atoms attached directly to it. Such repulsions may be minimized by appropriate rotation around the carbon–oxygen bond in acyclic compounds but not as easily in cyclic compounds. This electron repulsion effect operates in addition to the electronegativity effect, by which rates of formation of sp^2-hybridized carbanions are slowed by highly electronegative atoms attached directly to the site of carbanion formation. This interpretation of the results is analogous to that required to explain recent observations on rates of pyramidal inversions at nitrogen and phosphorus.

It has been suggested that highly electronegative substituents on unsaturated carbon tend to make a compound less stable than analogous species in which the substituents are attached to saturated carbon.[2] To test this hypothesis in cases where stabilizing π-resonance interactions between the substituents and the unsaturated carbon are minimized, the effect of α substituents on the rates of sodium methoxide catalyzed deuterium exchange of methyl esters was studied.[3] α-Fluorine and α-methoxy substituents were found to decrease the reactivity or to increase it by much smaller amounts than would be expected from a Taft equation correlation of the effect of a number of other substituents. Similar effects of α-fluorine and α-alkoxy substituents had been observed in all the cases of formation of sp^2-hybridized carbanions upon which literature data were found. In the smaller number of cases in which the formation of α-fluoro- and α-alkoxy-substituted sp^3-hybridized carbanions was studied, these substituents were found to increase the reactivity markedly (although perhaps not by as large a factor as would be expected from the inductive effect). An alternative (or additional) explanation for the deactivating effect of α-fluorine and α-alkoxy substituents on the formation of sp^2-hybridized carbanions is that there is a repulsive interaction between the unshared electron pairs of the substituent and the π electrons of the sp^2-hybridized carbon atom of the carbanion. The slower carbanion formation at the 2 position than at the 3 and 4 positions of pyridine has been explained in such terms,[4–7] as have the effects of α-halogen substituents on carbanion formation.[8] Attributing destabilization of carbanions by α-fluorine to a positive mesomeric effect[9] or to conjugative destabilization[10] may be equivalent. Such an explanation for the effect of α-methoxy and -fluoro substituents on the rate of deuterium exchange of methyl esters[2] had been considered, but it seemed to offer no explanation for why the deviation from the Taft equation correlation observed with a fluoro substituent ($10^{4.4}$-fold) was so much larger than that observed with a methoxy substituent ($10^{2.5}$-fold).[11] It is true that the smaller covalent radius of fluorine would bring the orbitals containing the unshared electrons closer to the negatively charged carbon than the analogous orbitals on oxygen in a methoxy substituent. However, it seemed unlikely that this would do much more than compensate for the more diffuse character of the orbitals bearing the unshared electrons on oxygen, resulting from the smaller nuclear charge of oxygen (*cf.* the larger van der Waals radius of oxygen). A potentially important factor that had been overlooked was the possibility that interactions between the π electrons of the carbanion and the unshared electrons of a methoxy substituent would be minimized by appropriate rotation around the bond between the sp^2 carbon and oxygen atoms. To obtain experimental data concerning this possibility, we have studied the deuterium exchange of methyl esters of cyclopentanecarboxylic acid and two of its oxa derivatives. Some reference compounds were also studied to give an idea of the significance of steric effects.

Results

The only methyl ester studied that was not already a known compound was methyl 1,3-dioxolane-2-carboxylate, which was prepared from 2-vinyl-1,3-di-

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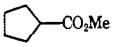
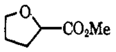
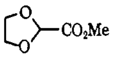
(9) A. I. Ivanov, V. I. Slovetskii, S. A. Shevelev, V. I. Erashko, A. A. Fainzelberg, and S. S. Novikov, *Zh. Fiz. Khim.*, 40, 2298 (1966); *Russ. J. Phys. Chem.*, 40, 1234 (1966).

(10) A. Streitwieser, Jr., and F. Mares, *J. Amer. Chem. Soc.*, 90, 2444 (1968).

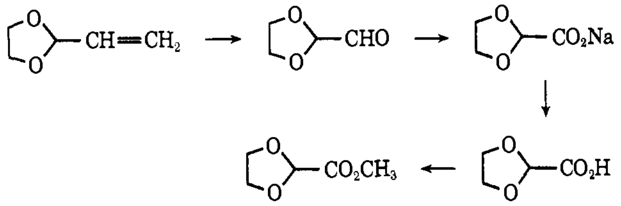
(11) These deviations from the Taft equation differ somewhat from those listed in the abstract of ref 3, which appear to be slightly in error.

Table I. Kinetic Data on the Sodium Methoxide Catalyzed Deuterium Exchange of Methyl Esters in Methanol-*O-d*[a]

Ester	10^6k, M^{-1} sec^{-1} 35°	60°	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
Me_2CHCO_2Me	9.95 ± 0.52	103 ± 6	18.4 ± 0.7	-20 ± 2
Et_2CHCO_2Me	1.95 ± 0.05	23.2 ± 0.5	19.5 ± 0.3	-19 ± 1
$MeOCH(Et)CO_2Me$	18.6 ± 2.7			
$(MeO)_2CHCO_2Me$	10.6 ± 0.9	159 ± 2	21.5 ± 0.7	-12 ± 2
	24.9 ± 1.0	453 ± 28	23.0 ± 0.6	-3 ± 2
	67.3 ± 3.5	688 ± 18	18.3 ± 0.5	-16 ± 2
	5.32 ± 0.32	55.5 ± 2.4	18.5 ± 0.6	-21 ± 2

[a] The ± figures listed are standard deviations.

oxolane[12] by ozonolysis to the aldehyde, silver oxide oxidation in basic solution to give sodium 1,3-dioxolane-2-carboxylate, acidification and extraction of the acid into ether, and esterification with diazomethane.



The kinetics of deuterium exchange were followed by a method similar to that used previously,[3] in which the appearance of protiomethanol in the methanol-*O-d* used as solvent was monitored by measurements of its infrared absorption band at about 3360 cm^{-1}. The rate constants for deuterium exchange obtained are presumably slightly smaller than the rate constants for carbanion formation because the intermediate carbanions must be captured occasionally by the protiomethanol present in the solvent. However, the deuterium content of the solvent was reasonably constant (always in the range 97–98% at the midpoint of the run), and so the rate constants observed should be good measures of the *relative* rate constants for carbanion formation. Since the first-order rate constants for exchange were previously found to be proportional to the sodium methoxide concentration for ten different esters,[3] second-order rate constants were obtained by dividing the observed first-order rate constants by the sodium methoxide concentration without necessarily making several runs at different sodium methoxide concentrations.

The second-order rate constants for deuterium exchange of the esters studied in the present investigation at 35 and 60° and the enthalpies and entropies of activation calculated from eq 1 are listed in Table I. As an independent measure of the electron-withdrawing power of the substituents present in three of the esters the ionization constants of the corresponding carboxylic acids were determined by potentiometric titration and are listed in Table II.

$$k = \frac{\mathbf{k}T}{h} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R} \qquad (1)$$

Table II. Ionization Constants of Carboxylic Acids in Water at 35° and Zero Ionic Strength[a]

Acid	pK_a
Tetrahydrofuran-2-carboxylic acid	3.74 ± 0.03
Dimethoxyacetic acid	2.92 ± 0.02
1,3-Dioxolane-2-carboxylic acid	2.97 ± 0.01

[a] The ± figures listed are standard deviations

Discussion

Our results are conveniently discussed in terms of a Taft equation plot of the 35° data in Table I and most of the data obtained previously.[3] Treating the esters as compounds of the type $YZCHCO_2Me$ and plotting log *k vs.* $\sigma_Y^* + \sigma_Z^*$ require some sort of rather arbitrary treatment of the data on cyclic esters. We have assigned the same values of $\sigma_Y^* + \sigma_Z^*$ to these compounds as to their acyclic analogs, which we have defined as those compounds that would result from hydrogenolysis of the ring at the bond furthest from the atom at which carbanion formation takes place. This method of evaluating the polar substituent effects is supported by the fact that when the largest number of polar substituents are present, *i.e.*, in the cases of methyl 1,3-dioxolane-2-carboxylate and methyl dimethoxyacetate, the corresponding carboxylic acids have p*K* values within 0.05 of each other. The values 1.79 and 3.08 were used for σ_{OMe}^* and σ_F^*, as in the previous work.[3] The line shown in Figure 1 is that obtained previously by least-squares treatment of the data on methyl acetate, propionate, butyrate, β-phenylpropionate, and succinate.

Let us compare the reactivities of the cyclic esters and their acyclic analogs. In the case of methyl cyclopentanecarboxylate and methyl α-ethylbutyrate, which have no α-oxygen substituents, the cyclic compound is 13 times as reactive as its acyclic analog. With methyl tetrahydrofuran-2-carboxylate and methyl α-methoxybutyrate, where one α-oxygen substituent is present, the cyclic compound is only four times as reactive as its acyclic analog. When two α-oxygen substituents are present, *i.e.*, with methyl 1,3-dioxolane-2-carboxylate and methyl dimethoxyacetate, the acyclic compound is twice as reactive as its cyclic analog. Stated alternatively, replacing the two β-methylene groups of methyl α-ethylbutyrate by oxygen atoms (to give methyl dimethoxyacetate) is accompanied by a fivefold increase in reactivity, but the same structural change in methyl cyclopentanecarboxylate (to give

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(12) V. Faass and H. Hilgert, *Chem. Ber.*, 87, 1343 (1954).

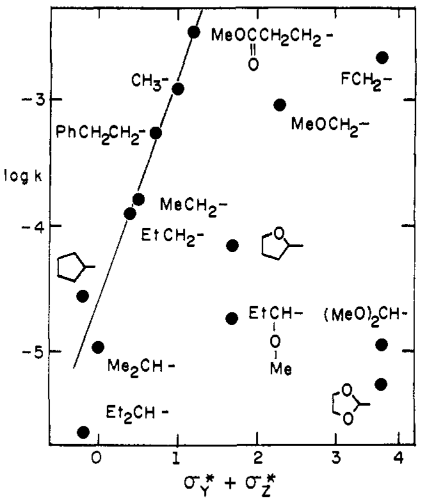
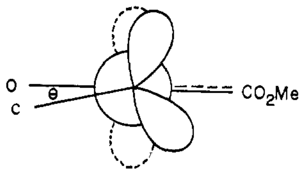


Figure 1. Log of rate constants, per α-hydrogen, for the methoxide ion catalyzed deuterium exchange of esters of the type **YZCHCO$_2$-Me** *vs.* $\sigma_Y^* + \sigma_Z^*$. Each point is labeled with the appropriate **YZCH-**.

methyl 1,3-dioxolane-2-carboxylate) gives a fivefold decrease in reactivity.

The decreased reactivity of the α-ethylbutyrate relative to that of the cyclopentanecarboxylate must arise in part from steric hindrance, the most plausible explanation for the negative deviation of the point for Et$_2$CH from the line in Figure 1. However, the positive deviation of the point for the cyclopentane compound from the line suggests that the reactivity of this compound is being increased by the relief of eclipsing strain that has been found to accompany the change of one of the atoms in a saturated five-membered ring from sp^3 to sp^2 hybridization.[13] This effect is presumably responsible for the greater acidity of cyclopentylbenzene than isopropylbenzene,[14] the more rapid base-catalyzed deuterium exchange of cyclopentyl phenyl ketone than isopropyl phenyl ketone,[15] etc. Since a methoxy substituent should be somewhat less bulky than an ethyl substituent, attack on the α hydrogen of methyl dimethoxyacetate should be somewhat less hindered than on that of methyl α-ethylbutyrate. Hence, the decrease in hindrance on going to the cyclic compound should also be somewhat smaller. Barriers to rotation around saturated carbon–oxygen bonds are ordinarily smaller than for saturated carbon–carbon bonds. This fact, which explains the highly flexible nature of 1,3-dioxolane rings,[16] leads one to expect less relief of strain on changing the hybridization of C-2 in the 1,3-dioxolane ring from sp^3 to sp^2. Thus, both the changes in steric hindrance and in conformational effects lead one to expect methyl 1,3-dioxolane-2-carboxylate to be less than 13 times as reactive as methyl dimethoxyacetate; however, they give no explanation for why it is *less* reactive.

A possible explanation for the decreased reactivity of the 1,3-dioxolane-2-carboxylate may be given in terms of repulsions between unshared electrons. Carbanion **1** is a Newman projection down the bond from one of the α oxygen atoms to the carbon atom from which a proton has been removed to give the carbanion. It may represent either methyl 1,3-dioxolane-2-carboxylate or methyl dimethoxyacetate, depending on what is attached to the carbon and oxygen atoms on the left.



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The oxygen atom is taken to be sp^3 hybridized, with two of the orbitals used for σ bonding and two for unshared electron pairs.[17a] The carbanionic carbon atom is taken to be sp^2 hybridized and to contain a significant electron density in the p orbital indicated by the dashed lines. Let us assume that between the electrons in this p orbital and those in either sp^3 orbital of oxygen there is a destabilizing interaction that decreases from a maximum when the dihedral angle between the axes of the orbitals is 0° to zero when the dihedral angle is 90°. Let us further assume that the magnitude of this destabilizing interaction is proportional to the square of the cosine of the dihedral angle.[17b] The total destabilizing energy may then be expressed (eq 2) in terms of the dihedral angle labeled θ in **1**. According to eq 2 the total destabilization energy decreases monotonically from 1.5C at a dihedral angle of 0° to 0.5C at a dihedral angle of 90°.

$$E = C(\cos^2\theta + 0.5) \qquad (2)$$

If the proportionality constant C is reasonably large, then the destabilization energies should be considerably smaller in the carbanion derived from methyl dimethoxyacetate, where the angle θ may be near 90° without introducing obvious strain, than in the carbanion derived from methyl 1,3-dioxolane-2-carboxylate, where the ring must force θ to assume smaller values (0°. when the ring is coplanar). In view of the other evidence for the importance of repulsions by unshared electrons on ease of carbanion formation,[4–10] the concept thus seems a plausible explanation for the lesser reactivity of the five-membered ring compound in the case where there are two oxygen atoms attached to the site at which carbanion formation occurs.

We have estimated that in the absence of unshared electron repulsions methyl 1,3-dioxolane-2-carboxylate would be less than 13 times as reactive as methyl dimethoxyacetate. Since in fact it is half as reactive, we are attributing a change in reactivity of less than 26-fold to unshared electron repulsion. This is small relative to the factor of 10^7-fold by which the point for the 1,3-dioxolane-2-carboxylate deviates from the line in Figure 1. It seems doubtful that unshared electron repulsion would produce such a large deviation from the linear free-energy relationship depicted in the figure without producing a larger difference in reactivities

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(17) (a) The unshared electrons could be resolved into two other appropriately hybridized orbitals, such as a p orbital and an sp orbital, without changing the results, of course. (b) When this treatment is applied to an α-fluoro carbanion, where there are three sp^3 orbitals containing unshared electron pairs, the calculated energy is a constant. The fact that the energy does not change when the set of three orbitals is rotated around the carbon–fluorine bond fits the fact that any choice among the rotomeric possibilities would be completely arbitrary.

between the 1,3-dioxolane-2-carboxylate and the dimethoxyacetate. Hence there still seems to be a need to invoke the electronegativity argument used previously.[3]

The preceding conclusions are in line with recent observations on rates of inversion of pyramidal nitrogen and phosphorus compounds. The idea that electronegative substituents should stabilize the pyramidal forms of such species relative to the planar forms[18] has been supported by measurements of inversion rates at nitrogen and by quantum mechanical calculations.[19–23] The rates of inversion of phosphorus compounds of the type $PhP(R)MMe_3$, where M was C, Si, Ge, or Sn, provide particularly strong evidence for the electronegativity effect because the MMe_3 groups contain no unshared electrons.[24] The importance of repulsions of unshared electrons is suggested by the fact that the rate of inversion of an *N*-methylpyrrolidine is decreased more by replacing a nitrogen-bound ring methylene group by oxygen than by replacing the methyl group by hydroxyl.[21] The hydroxy group could orient itself so as to minimize repulsions between unshared electron pairs more easily than an endocyclic oxygen atom could.

Since α-alkoxy and α-fluorine substituents stabilize pyramidal carbanions more than they stabilize planar carbanions,[3,25] the introduction of such substituents could cause the geometry of the carbanions being formed from a given series of compounds to change from planar to pyramidal. Streitwieser and Mares have proposed on the basis of reactivity data that the introduction of two α-fluoro substituents changes the planar benzyl anion to a pyramidal α,α-difluorobenzyl anion.[10] If the stability of the pyramidal form of a carbanion relative to its planar form becomes large enough, the phenomenon of hydrogen exchange with retention of configuration should become observable. There is some evidence that it has not become so in the case of methyl α-methoxypropionate. This compound was found to undergo sodium methoxide catalyzed racemization in methanol with a rate constant of $8 \times 10^{-6}\ M^{-1}\ \text{sec}^{-1}$ at 24.7°.[27] If methoxide ions in methanol-*O-d* are about 66% more reactive in this case, as they are in displacing halide ions from methylene halides,[28] and if the activation energy is in the range of those listed in Table I, this rate constant would be about $43 \times 10^{-6}\ M^{-1}\ \text{sec}^{-1}$ in methanol-*O-d* at 35°. The rate constant for deuterium exchange of methyl α-methoxypropionate at 35° may be estimated by comparison with the value for methyl α-methoxybutyrate. Since the latter has an α-ethyl substituent where the former has an α-methyl substituent the differences in log *k* might be expected to be about half the difference between log *k* for methyl isobutyrate, which has two α-methyl substituents, and methyl α-ethylbutyrate, which has two α-ethyl substituents. This gives a value of $42 \times 10^{-6}\ M^{-1}\ \text{sec}^{-1}$ for the rate constant for deuterium exchange, which, like the estimated rate constant for racemization, may easily be in error by 25%, but which agrees well enough with the rate constant for racemization to support a planar structure (or a pyramidal one that inverts rapidly) for the carbanion formed from methyl α-methoxypropionate.

We have rationalized the effect of unshared electrons in terms of two regions of high density of unshared electrons on either side of the plane of the two bonds to oxygen and a region of lower unshared electron density near the plane. This contrasts with the representation used by Wolfe and coworkers for at least one oxygen compound, in which there is assumed to be no decrease in unshared electron density near the plane of the two bonds.[29] In the argument leading to this representation interactions between unshared electron pairs on adjacent atoms are said to influence the conformation of the bond between the atoms less than bond–bond interactions do. It is pointed out, for example, that in hydrazine and hydrogen peroxide the lower energy barrier is the one that "*has the smaller number of nucleus–nucleus, i.e. bonded electron pair–bonded electron pair interactions.*"[29] This is true, but it is also true, of course, that these same barriers are the ones with the smaller number of unshared electron pair–unshared electron pair interactions. Wolfe and coworkers[29,30] discuss conformation rates and equilibria in terms of the " '*gauche effect,' i.e., a tendency to adopt that structure which has the maximum number of gauche interactions between the adjacent electron pairs and/or polar bonds.*"[30] This generalization is in accord with a number of experimental observations, but the statement that the gauche conformation is more stable for X_2CHCHX_2, where X is F, Cl, Br, or O,[30] disagrees with the reference given to gas-phase data on *sym*-tetrafluoroethane, whose trans form is about 1.16 kcal/mol more stable than the gauche,[31] and on *sym*-tetrachloroethane, whose gauche and trans forms are about equally stable.[31] Thus, with these compounds the generalization concerning the effect of polar bonds on conformation works more poorly with the more polar carbon–halogen bond. The facts are explained[32] at least qualitatively in terms of the tendency for Cl–C–Cl angles to be larger[33] but F–C–F angles smaller[34] than tetrahedral.

Experimental Section

Reagents. Each of the esters used was found by glpc on a 6-ft diethylene glycol succinate (DEGS) column to be at least 99.4% pure. Methanol-*O-d* was prepared from dimethyl carbonate.[35]

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Methyl 1,3-Dioxolane-2-carboxylate. Attempts to prepare 1,3-dioxolane-2-carboxylic acid or its methyl ester from glyoxylic acid and ethylene glycol and from methyl dichloroacetate and the sodium salt of ethylene glycol were unsuccessful, but we later learned that the former method has been made to work by Newman and Chen.[36]

Our successful method began by bubbling excess ozone through a solution of 8.5 g (85 mmol) of 2-vinyl-1,3-dioxolane[12] in 100 ml of methanol at −15°. The resulting solution was added to 150 ml of 5% aqueous sodium hydroxide and 42 g (180 mmol) of silver oxide. After 1 hr of rapid stirring the solution was filtered and the filtrate extracted with 100 ml of ether. Excess carbon dioxide was bubbled into the aqueous layer which was then evaporated to dryness at 20 mm pressure. The 26.5 g of white solid was extracted with hot methanol and the filtered methanol solution evaporated to dryness, leaving 10.5 g of white crystals whose nmr spectrum in deuterium oxide indicated the presence of equimolar amounts of sodium formate (δ 7.2) and sodium 1,3-dioxolane-2-carboxylate [δ 2.78 (s, 4, CH_2) and 3.88 ppm (s, 1, CH)].[37]

Enough 18 N sulfuric acid was added to 7.5 g of an equimolar mixture of sodium formate and sodium 1,3-dioxolane-2-carboxylate in 20 ml of water at 0° to give a pH of 2. The solution was quickly extracted twice with 100-ml portions of ether to which ethereal diazomethane was added until the yellow color persisted for 1 hr. Distillation of the magnesium sulfate dried solution gave 3.1 g of methyl 1,3-dioxolane-2-carboxylate: 99.4% pure by glpc (6-ft DEGS column); bp 87–88° (24 mm); nmr (CCl_4) δ 5.22 (s, 1, CH), 4.00 (br s, 4, CH_2), 3.70 ppm (s, 3, CH_3);[38] ir (neat) in order of decreasing intensity 1740, 1130, 1222, 940, 1035, 2955, 1292, 1420, and 2900 cm^{-1}.

Kinetics. The following changes were made in the kinetic procedure used previously.[3] A Perkin-Elmer grating spectrophotometer, Model 337, was used with 0.05 mm IR Trans II cells. Under these conditions, the extinction coefficient for MeOH, which was found to follow eq 3, was somewhat smaller than that

$$\epsilon_{\mathrm{MeOH}} = (108.8 - 5.98[\mathrm{NaOMe}])M^{-1}\ \mathrm{cm}^{-1} \qquad (3)$$

obtained previously. The runs at 60° were carried out by using a 2-ml sealed ampoule for each point. Ester concentrations were in the range 0.55–0.98 M and sodium methoxide concentrations in the range 0.36–0.62 M.

pK Determinations. The pK of tetrahydrofuran-2-carboxylic acid was determined by measuring the pH in a potentiometric titration against standard aqueous sodium hydroxide using a Radiometer titrator (ABU1, PHM26c, SBR2c, and type C electrode). The other two acids were used in the form of their sodium salts, which were titrated rapidly with standard acid (although reference data on other acetals show that no significant amount of hydrolysis of the acetal linkages would have occurred even under more acidic conditions). The ionic strengths at which the pH values were measured were in the range 0.005–0.020 M. The observed pH was taken to be $-\log a_{\mathrm{H}^+}$ and ionic activity coefficients were assumed to obey the Davies equation (*i.e.*, eq 4 at 35°). In

$$\log \gamma = 0.52\left(\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.2\mu\right) \qquad (4)$$

calculating the pK values proper allowance was made for the fact that the hydrogen ion concentrations were not negligible compared to the concentrations of the acid and its anion. The sodium salts used were prepared by recrystallizing from alcohol the products of the reaction of aqueous sodium hydroxide with the corresponding methyl esters. A weighed amount of each sodium salt was dissolved in deuterium oxide containing a known concentration of *tert*-butyl alcohol, the ratios of the areas of the strongest nmr peaks were found to agree with the calculated value, and no nmr peaks due to impurities could be seen.

Acknowledgment. We are indebted to Dr. Wendel Lim for carrying out preliminary studies on this investigation.

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(38) Chemical shifts downfield from internal tetramethylsilane.

Effect of Solvent on the Ground States and Transition States in the Reactions of 2,4,6-Tri-*tert*-butylphenoxyl with Phenols

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Abstract: The absolute rate constants for the hydrogen atom transfer reaction of the 2,4,6-tri-*tert*-butylphenoxyl radical with phenols in various solvent systems have been determined at 30 and 60°. The Henry's law constants for phenol and 1,3,5-tri-*tert*-butylbenzene which had previously been shown to be a good model for the solution properties of the free radical have been determined by transpiration techniques. Utilizing infrared spectroscopy, the activity coefficients of Prigogine for the specific hydrogen bonding interactions of phenol with solvent have been determined. The results of these kinetic and solution property studies have been combined and subjected to a detailed analysis based upon activity coefficients. This type of analysis provided a detailed description of the partial molal energy changes resulting from the transfer of the activated complex, free radical, and phenol from carbon tetrachloride to other solvent systems. The findings suggest that the mechanism of the reaction involves a prior equilibrium formation of a hydrogen-bonded free radical–phenol complex, followed by hydrogen atom transfer within the complex. It is shown that this mechanism accounts for the abnormally low activation energies observed for hydrogen atom transfer between oxyl radicals and is consistent with the A factors observed for such reactions. Finally, the effect of solvent on such reactions is not consistent with the activated complex being polar in nature.

An important reaction in a number of free-radical systems is the transfer of hydrogen atoms between oxy radicals. For example, the mechanism of the phenolic inhibition of hydrocarbon oxidation involves the rapid and often reversible transfer of hydrogen atoms between phenoxy and peroxy free radicals.[1]

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(1) For a review, *cf.* L. R. Mahoney, *Angew. Chem. Int. Ed. Engl.*, 8, 547 (1969).